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Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M.

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Light intensity dependence of open-circuit voltage of polymer:fullerene solar cells

L. J. A. Koster,[a] V. D. Mihailetchi, R. Ramaker, and P. W. M. Blom
Materials Science Centre[Plus], University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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The open-circuit voltage V_{oc} of polymer:fullerene bulk heterojunction solar cells is investigated as a function of light intensity for different temperatures. Devices consisted of a blend of a poly (*p*-phenylene vinylene) derivative as the hole conductor and 6,6-phenyl C_{61}-butyric acid methyl ester as the electron conductor. The observed photogenerated current and V_{oc} are at variance with classical $p-n$ junction-based models. The influence of light intensity and recombination strength on V_{oc} is consistently explained by a model based on the notion that the quasi-Fermi levels are constant throughout the device, including both drift and diffusion of charge carriers. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1889240]

Organic photovoltaic elements are a promising alternative to conventional inorganic solar cells because of their low-cost fabrication of large areas. The best performance is currently obtained with polymer:fullerene bulk heterojunction solar cells,[1] yielding power conversion efficiencies of typically 2.5% under AM1.5 illumination. One of the key parameters of photovoltaic devices is the open-circuit voltage (V_{oc}), which is the voltage for which the current in the external circuit equals zero. In polymer:fullerene solar cells limitations of the open-circuit voltage have been attributed to Fermi level pinning[2] and to band bending at the contact due to the injection of charges.[3] For further optimization of solar cell performance fundamental understanding of the mechanisms governing the photovoltaic performance is indispensable.

For a conventional (Si) $p-n$ junction solar cell the current density under illumination J_L is given by[4]

$$J_L = J_s(e^{qV/nkT} - 1) - J_{ph}, \tag{1}$$

where J_s is the (reverse bias) saturation current density, V is the applied voltage, q is the elementary charge, k is Boltzmann's constant, T is temperature, and n is the ideality factor. The photogenerated current density is denoted by J_{ph}. Subsequently, the open-circuit voltage is given by $(J_L=0)$

$$V_{oc} = (nkT/q)\ln(J_{sc}/J_s + 1), \tag{2}$$

where J_{sc} is the short-circuit current density. It should be noted that Eq. (2) is only valid for an ideal solar cell since it has been assumed that the photogenerated current density is voltage independent, meaning that $J_{ph}=J_{sc}$ at any applied voltage. Recently, Eq. (2) has also been applied to explain the temperature dependence of V_{oc} of polymer:fullerene bulk heterojunction solar cells.[5,6] However, it is not clear whether such an analysis in terms of an ideal solar cell is justified for the case of polymer:fullerene bulk heterojunctions. Moreover, the fact that both J_{sc} and J_s are also temperature dependent further complicates the applicability of Eq. (2) to the effects of temperature on the device characteristics of organic bulk heterojunction devices. A more direct way of testing the applicability of Eq. (2) toward organic solar cells is to investigate the dependence of V_{oc} on light intensity at different temperatures. Since it has been demonstrated that J_{sc} is nearly linearly dependent on light intensity,[7,8] it follows from Eq. (2) that V_{oc} should exhibit a slope of nkT/q, when plotted as a function of the logarithm of light intensity. In this study we demonstrate that the light intensity dependence of V_{oc} of polymer:fullerene bulk heterojunction solar cells is in contradiction with the predictions of the conventional $p-n$ junction based model [Eq. (2)]. An alternative expression for V_{oc} is presented that is based on the fact that at zero current the quasi-Fermi levels are constant throughout the device, which incorporates both drift and diffusion of charge carriers. This expression consistently explains the experimental dependence of V_{oc} on light intensity for bulk heterojunction devices.

The solar cells addressed in this study are bulk heterojunctions consisting of a blend of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylenevinylene] (MDMO-PPV) as electron donor and 6,6-phenyl C_{61}-butyric acid methyl ester (PCBM) as electron acceptor in a 1:4 weight ratio. This blend is sandwiched between a hole-conducting layer of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS), and an evaporated lithium fluoride (LiF) (1 nm)/aluminum (100 nm) top electrode. After fabrication the current–voltage characteristics of these devices were measured in a nitrogen atmosphere, both in dark and under illumination. A white light halogen lamp set at 800 W/m^2 (spectral range 450–750 nm) was used to illuminate the devices. Incident light power dependent measurements were performed by using a set of six neutral density filters with a constant optical density in the involved spectral range. The generation rate of electrons and holes is assumed to be proportional to the intensity.

In Fig. 1 the dark current density J_{dark} is shown as a function of voltage V for a MDMO-PPV:PCBM based solar cell at different temperatures. From the slope of the exponential part of the $J-V$ characteristics the ideality factors are determined. The results are summerized in Table I. At room temperature the ideality factor n typically amounts to 1.4 and then further increases to 2.0 at 210 K, in agreement with other observations.[9] Subsequently, the current–voltage characteristic (J_L-V) of an illuminated (800 W/m^2) device at room temperature is shown in Fig. 2, together with the current predicted by Eq. (1). It is clear that there is a large

[a]Electronic mail: l.j.a.koster@rug.nl

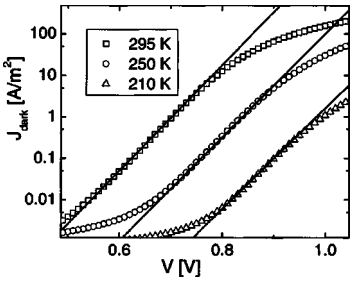

FIG. 1. Experimental dark current of a MDMO-PPV:PCBM device (symbols) and fit to the exponential part (lines) at various temperatures.

discrepancy between the predictions of the model and the experimental data: near V_{oc} the predicted current is much too high. This already strongly indicates that the $p-n$ junction model is not applicable to polymer:fullerene bulk heterojunction devices. Figure 3 shows V_{oc} as a function of the logarithm of light intensity at various temperatures, the highest intensity corresponds to 800 W/m^2 (no filter). The experimental data are fitted with a linear function with slope S which is given in Table I in units of kT/q. Suprisingly, the experimental slopes are within experimental error equal to kT/q instead of nkT/q [Eq. (2)] for all temperatures. Thus, next to the photocurrent (Fig. 2) the light intensity dependence of V_{oc} is also not in agreement with the classical model. It should be mentioned that we have also verified this for other PPV derivatives.

The main reason for this disagreement is that, as stated previously, Eq. (2) is based on the assumption of a voltage-independent photogenerated current J_{ph}. Recently, it has been shown by Mihailetchi *et al.*[10] that the photogenerated current of MDMO-PPV:PCBM devices shows a very different behavior: In the inset of Fig. 2 the photogenerated current of such a device is plotted as a function of effective applied voltage, $V_{oc}-V$, where V_{oc} has been corrected for dark current. Near the open-circuit voltage, a linear dependence of the photogenerated current upon applied voltage is observed. This behavior is caused by the opposite effect of drift and diffusion of charge carriers.[11] At V_{oc} drift and diffusion balance and the current is zero. At higher effective voltage $V_{oc}-V>0.1$ V the drift contribution is dominant and the photogenerated current tends to saturate. However, due to an increased dissociation efficiency of photogenerated bound electron–hole pairs, the photocurrent further increases before it reaches full saturation at $V_{oc}-V>10$ V.[10] Consequently, the assumption of a constant photogenerated current is not valid. When the photocurrent near the open-circuit voltage is

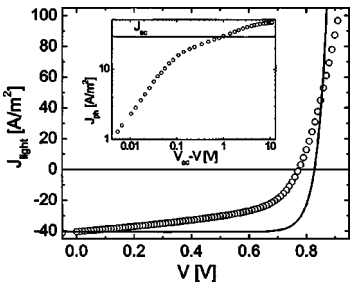

FIG. 2. Experimental current under illumination of an MDMO-PPV:PCBM device at 295 K (symbols) and the current density predicted by Eq. (2) (line). Inset: The photogenerated current density J_{ph} of an MDMO-PPV:PCBM device (symbols) as a function $V_{oc}-V$. The line denotes the short-circuit current density corresponding to the assumption of J_{ph} being constant.

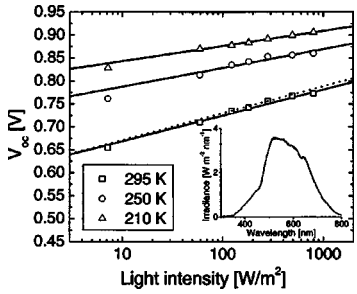

FIG. 3. V_{oc} of a MDMO-PPV:PCBM device (symbols) as a function of light intensity, the solid lines denote linear fits to the experimental data, and the dotted line represents the prediction at room temperature of Eq. (12). The inset shows the spectrum of the white light halogen lamp used to illuminate the devices.

equated to J_{sc} (inset of Fig. 2, line) the photocurrent is strongly overestimated, hence Eq. (2) cannot be expected to meticulously reproduce the experimental data. We note that the fit of Eq. (1) to experimental photocurrent data is often improved by including series and shunt resitivities.[9] However, the physical meaning of these quantities is not clear though.

We suggest an alternative expression for the open-circuit voltage, based on the metal–insulator–metal picture.[12] In this approach, the device is described as one semiconducting material with the highest occupied molecular orbital (HOMO) of the polymer functioning as the valence band and the lowest unoccupied molecular orbital (LUMO) of PCBM acting as conduction band. The energy difference between the HOMO and LUMO levels will be denoted by the band gap E_{gap}. As a first step, the quasi-Fermi levels $\varphi_{n,p}$ are introduced as[13]

$$n(p) = n_{int} \exp[(-)q(V-\varphi_{n(p)})/(kT)], \tag{3}$$

where $n(p)$ is the electron (hole) concentration under illumination and n_{int} is the intrinsic concentration of both electrons and holes. The intrinsic carrier concentration n_{int} is given by

$$n_{int} = N_c \exp(-E_{gap}/(2kT)), \tag{4}$$

where N_c is the effective density of states, which is equal to 2.5×10^{25} m^{-3}.[14] The product np is known to statisfy $np = n_{int}^2$ in equilibrium,[15] however,

$$np = n_{int}^2 \exp[q(\varphi_p-\varphi_n)/(kT)], \tag{5}$$

when the system is not in equilibrium. The familiar expression for the electron (hole) current density, including both drift and diffusion, is,[6]

$$J_{n(p)} = q\mu_{n(p)}n(p)E + (-)kT\mu_{n(p)}\frac{\partial}{\partial x}n(p), \tag{6}$$

where $\mu_{n(p)}$ is the electron (hole) mobility and E is the electric field strength. Equation (6) can be rewritten in terms of the quasi-Fermi levels as[6]

TABLE I. Overview of ideality factors n obtained from Fig. 1 and slopes S obtained from Fig. 3.

	295 K	250 K	210 K
n	1.34	1.62	1.98
$S(kT/q)$	1.03	1.01	0.90

$$J_{n(p)} = -q\mu_{n(p)}n(p)\frac{\partial}{\partial x}\varphi_{n(p)}. \quad (7)$$

At open circuit the current densities are (virtually) zero, consequently, the quasi-Fermi levels are constant. Since the (ohmic) contacts are in thermal equilibrium, the quasi-Fermi levels have to be equal to the potential at the contacts. This implies that the difference $\varphi_p - \varphi_n$ is constant throughout the device and equal to the applied voltage at open-circuit, therefore

$$np = n_{\text{int}}^2 \exp[qV_{\text{oc}}/(kT)]. \quad (8)$$

We have recently developed a numerical model succesfully describing the current–voltage characteristics of polymer:fullerene solar cells which includes drift and diffusion of charge carriers, bimolecular recombination, and the effect of field- and temperature-dependent generation of free charge carriers.[16] In this model the continuity equation for electrons is given by

$$\frac{1}{q}\frac{\partial}{\partial x}J_n(x) = PG - (1-P)R, \quad (9)$$

where P is the dissociation probability of a bound electron–hole pair into free charge carriers, G is the generation rate of bound electron-hole pairs, and R the Langevin recombination rate of free electrons and holes given by

$$R = \gamma(np - n_{\text{int}}^2), \quad (10)$$

where γ is the Langevin recombination constant. The generation rate of free charge carriers is then represented by PG. The recombination rate can be written as, to a very good approximation, $R = \gamma np$, since the photogenerated charges outnumber the thermally excited charge carriers by many orders of magnitude [see Eq. (8)]. Since the current densities are zero, so are their derivatives and hence recombination and generation cancel everywhere in the device. Subsequently, it follows from Eq. (9) that,

$$G = \gamma np(1-P)/P. \quad (11)$$

Therefore, using Eq. (8) and solving for V_{oc} one has

$$V_{\text{oc}} = \frac{E_{\text{gap}}}{q} - \frac{kT}{q}\ln\left(\frac{(1-P)\gamma N_c^2}{PG}\right). \quad (12)$$

This formula predicts the right slope S of V_{oc} versus light intensity, viz., kT/q, since P and γ do not depend on intensity. Further, Eq. (12) is consistent with the notion of a field-dependent photogenerated current, in contrast to Eq. (2), since both drift and diffusion have been taken into account through the use of Eqs. (6) and (7). Using the appropriate values for the electron and hole mobility for an MDMO-PPV:PCBM device,[16] $E_{\text{gap}} = 1.3$ eV (corresponding to an energy difference between the HOMO of MDMO-PPV and the LUMO of PCBM of 1.3 eV[16]), $P = 0.474$,[16] $N_c = 2.5 \times 10^{25}$ m^{-3},[16] and $G = 2.7 \times 10^{27}$ m^{-3} s^{-1} for the generation rate, corresponding to illumination by a white light halogen lamp (spectrum shown in inset of Fig. 3) set to 800 W/m^2,[9] Eq. (12) predits $V_{\text{oc}} = 0.8$ V at room temperature. This is in good agreement with the corresponding experimental value of 0.77 V as shown in Fig. 3. Figure 3 also shows the predicted light intensity dependence of V_{oc} as predicted by Eq. (12) (dotted line). It should be noted that the analysis of the temperature dependence of V_{oc} of polymer:fullerene solar cells by using Eq. (12) is strongly complicated by the absence of a sharply defined band gap. Due to the presence of energetic disorder in both materials, their HOMO and LUMO levels exhibit a Gaussian broadening σ of typically 0.1 eV.[17,18] Since the exact distribution of energy levels inside the PPV:PCBM blend is not known, the uncertainty in E_{gap} is of the same order of magnitude as the variation of V_{oc} with temperature, thereby prohibiting an exact quantitative analysis. For further analysis temperature-dependent charge transport measurements performed on blends are necessary.

In summary, we have investigated the open-circuit voltage at various temperatures and demonstrated that the open-circuit voltage, when plotted as a function of light intensity, has a slope equal to kT/q. This cannot be explained by using a formula derived from $p-n$ junction-based models for current–voltage characteristics in dark and under illumination. The main cause of this discrepancy lies in the fact that the strong voltage dependence of the photogenerated current is not taken into account. An alternative model for the open-circuit voltage has been presented, based on the notion that the quasi-Fermi levels are constant throughout the device. This model consistently explains the light intensity dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction devices.

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